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RESEARCH

Phthalocyanine green aluminum pigment prepared by inorganic acid radical/radical polymerization for waterborne textile applications

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Abstract Polymer-encapsulated phthalocyanine green aluminum pigment was prepared via inorganic acid radical/radical polymerization route, and its properties were investigated by FT-IR, TGA, XPS, SEM, and TEM. SEM and TEM images showed that the aluminum pigment was encapsulated by a thin film of polymer which ensured good anti-corrosive performance in alkaline (pH 12) and acidic (pH 1) mediums. XPS results showed significant chemical shifts, and increase in binding energies to higher levels after raw aluminum pigment was phosphate coated and colored by phthalocyanine green pigment. TGA results suggest a marginal reduction in its thermal stability. Major absorbance peaks, such as aluminum phosphate ($AlPO_4$), different monomer units and CH_2 stretching vibration of phthalocyanine green G were highlighted in the FTIR spectra of the colored aluminum matrix. The polymer-encapsulated aluminum pigment (PAP) had excellent UPF properties regardless of the coating thickness, but the handle of the fabric was affected when the coating thickness increased beyond 0.04 mm. The prepared pigment showed excellent rubbing and washing fastness, but its handle and color strength were compromised when the content of monomer ratio by 100 % weight of PGAP increased beyond 10 %, was applied on cotton fabrics. This research provides a simple but effective route for the preparation of polymer-encapsulated aluminum pigments for waterborne textile applications.

Keywords Aluminum pigment · Phthalocyanine green · Polymer encapsulation · Radical polymerization · Inorganic acid radical

Introduction

Colored aluminum pigments having colorful pigment adhered closely, uniformly and firmly on its surface are suitably used in paints, automotive metallic finish, printing inks, molded resins and in decoration finish of plastics [1–3]. The application of aluminum pigment has expanded into security services, including the military, due to its high emissive properties and the ability to reflect IR rays in the solar spectrum [4–7]. Recently, colored aluminum pigments have been used in plastic components of objects, such as boats or buoys, to make them visible to RADAR detection due to their ability to reflect in the electromagnetic radiation [5, 8]. These and many other functional properties of aluminum pigments have rekindled research interest lately.

Traditionally, colored aluminum pigments are prepared by physically mixing colorful pigments with silver white aluminum pigments which makes it difficult to achieve vivid color tones because, the achromatic tone inherent in aluminum pigment is usually emphasized [2, 9, 10]. These pigments are usually common in the automotive industry where volatile organic compounds (VOCs) are commonly used as the medium for their application. These pigments, however, are not suitable for textiles applications where water play a major role throughout the manufacturing process to the care phase, hence the need to develop

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waterborne colored aluminum pigment for textiles applications. To surmount these problems, several techniques have been proposed as a solution to obtaining waterborne colored aluminum pigment by depositing pigment onto the surface of an aluminum pigment with the aid of polymeric coatings [9, 11–13]. Other researchers have suggested a route where silica is coated onto aluminum pigment using sol-gel method followed by color deposition with the aid of surface modification agents [9, 10], but the issue of corrosion and color deformation still persisted after a long exposure to high alkaline waterborne systems. As a result, the use of colored inorganic flaky materials, such as mica flakes, has been suggested [13–15]; which gives a pearly color tone of their own. The use of popular techniques, such as metal organic chemical vapor deposition, physical vapor deposition, laser cladding, and thermal spraying, has also been thoroughly investigated [16–18]. Meanwhile, drawbacks such as low hiding power, poor metallic luster, and lack of color vividness have persisted because of the difficulty in depositing ample amount of colorful pigment onto the surface of aluminum pigment [7, 12].

Recently, the traditional wet chemical coating methods using silica-coated aluminum pigments (Al/SiO_2) or phosphates as precursor materials with dyes have been reported [19, 20], but problems such as poor corrosive stability, color fading, and complicated preparation process have still remained [1, 9, 21]. The use of inorganic acid radical for coating aluminum pigment has been reported to enhance its corrosion protection ability and ensure uniform coating [12, 22–24] hence its extensive application in corrosion chemistry. Meanwhile, the application of inorganic radical/radical polymerization for coloring silver white aluminum pigment with phthalocyanine green G has not been reported.

The main object of this research is to provide aluminum pigment colored to the highest chroma by depositing phthalocyanine green G pigment on the surface of aluminum pigment, thereby improving the chroma and avoiding the issue of color fading and exfoliation inherent in conventionally pigment colored aluminum pigments. To achieve these objectives, a colorful pigment (phthalocyanine green G) with inherently high tinctorial strength and excellent fastness to different solvents, heat, light, weathering [15, 25] was chosen and adsorbed onto aluminum pigment having adsorption layer of inorganic acid radical with the green colorful pigment adhered to said adsorption layer. The phthalocyanine green G colored aluminum pigment was then coated with a polymer using radical polymerization, and its properties were investigated. The application of both techniques overcome the limitations of classical polymerization and corrosion inhibition methods and provides an efficient route for preparing colored aluminum pigment having excellent properties.

Experimental

Materials

Aluminum pigment (particle size 50 μm) was purchased from Tianjiu Metal Materials Co., Ltd., Changsha, China. Allyloxy nonyl alcohol polyoxyethylene (10) ether sulfate (DNS-86), sodium dodecyl sulfate (SDS), *N*-l3-(aminoethy1)-y-aminopropylmethyldimethoxysilane (Silane Si–602) (structure is shown in chat 1b) were purchased from Qingxin Haner Chemical Technology Co. Ltd., China. Binder (DM-5218), thickener (DM-5268) and crosslinker (FWO-B) were purchased from Demei Chemical Company Ltd. Phthalocyanine green G (purity 97 %) (Structure shown in chat 1a) was purchased from Anping Guanda Pigment industry Co. Ltd., China. Other analytical grade chemicals, such as methylmethacrylate, 1,6-hexanedio1 diacrylate, styrene (ST), azobisisobutyronitrile (AIBN), isopropyl alcohol, polyphosphoric acid, surfynol 440, acetone, absolute ethanol, sodium hydroxide, and methanol, were supplied by Sinopharm Chemical Reagent Co. Ltd., China and were used without further purification. Deionized water was used for the entire experiments (see Fig. 1).

Pretreatment of aluminum

The aluminum pigment was washed with acetone and dried at 70 °C in vacuum oven for 6 h.

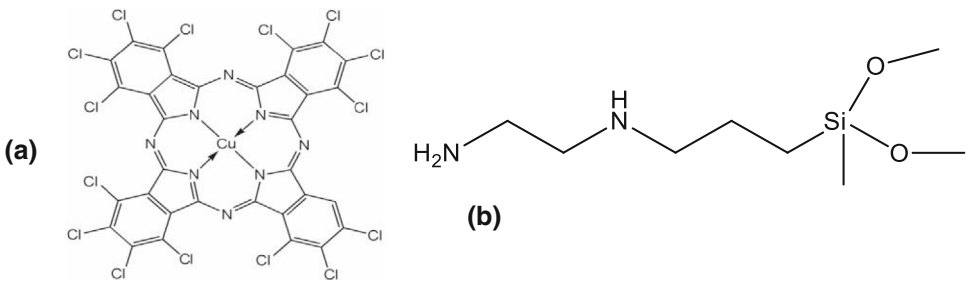


Fig. 1 Structure of (**a**) phthalocyanine green G (**b**) *N*-l3-(aminoethy1)-y-aminopropylmethyldimethoxysilane

Pigment dispersion

10 g SDS and DNS-86 in the ratio 1:1 based on 10–30 % weight of pigment (phthalocyanine green G) were mixed in 150 g deionized water. 1 g of glycerol and 6 g of *N*-l3-(aminoethy1)-y-aminopropylmethyldimethoxysilane were added and then subjected to mechanical stirring for 30 min at 450 r/m after which the pH was adjusted to 9. The pigment was further dispersed using bead mill Mini Zeta-03-E NETZSCH Grinding & Dispersing Machine (Germany) at 1800 r/m for 2 h to obtain finely dispersed phthalocyanine green G pigment with average particle size of 118 d nm. The dispersion was filtered through 0.5 μm pore-filtering sieve to remove broken pieces of glass beads.

Preparation of inorganic acid radical coating

12 g of aluminum pigment was dispersed in 80 g isopropyl alcohol using ultrasonicator JY98-3D, NingBo Scientz Biotechnology Co., Ltd, China at frequency of 28 kHz and power of 400 W for 10 min to obtain aluminum dispersion. 2 g of polyphosphoric acid (1 part by weight on the basis of 100 parts by weight of aluminum pigment) and 1 g of surfynol 440 were added, and the resultant mixture was kneaded for 1 h to adsorb the polyphosphoric radical to the surface of the aluminum pigment.

The aluminum pigment adsorbing inorganic acid radical prepared in step (see "Preparation of inorganic acid radical coating") was added to the dispersion of color pigment prepared in step (see "Pigment dispersion") to obtain aluminum pigment/color slurry. 20 g alcohol/water mixture was added to the slurry and stirred for 5 h. The slurry was subjected to solid–liquid extraction to obtain colored aluminum precipitates. The precipitates were dried at 60 °C for 6 h to obtain phthalocyanine green colored aluminum pigment (PGAP).

Radical polymerization

10 g of colored aluminum pigment was dispersed in 100 g toluene using ultrasonicator. The ultrasonicated colored aluminum pigment was transferred to a four-necked round bottom flask with a reflux condenser and a nitrogen gas inlet/out-let in a water bath equipped with thermometer (60 °C) with continuous stirring at 300 r/m. 0.3 g each of methyl methacrylate, 1,6-hexanediol diacrylate, styrene were added drop by drop over 1 h. 0.04 g of polymerization initiator (AIBN) was added thereunto drop by drop, and the temperature was raised to 85 °C with continuous stirring at 450 r/m for 20 h. The mixture was allowed to cool to room temperature and then centrifuged at 12,000 r/min for 10 min. The sediment was washed three times with methanol to remove the unreacted monomers and then dried at room temperature under vacuum to obtain polymer-encapsulated PGAP.

Fabric coating

The coating paste was formulated on the following weight basis: polymer-encapsulated PGAP 22 %, glycerol 1 %, DM-5268 3 %, urea 0.3 %, FWO-B 4 %, DM-5218 23.7 %, and distilled water 50 %. These components were mixed to obtain a homogenous paste. Cotton fabrics obtained from Shandong Weiqiao Pioneering Group Co., Ltd, China were coated using rapid auto coat machine from Xiamen Rapid Company Ltd, China. The coated fabrics were dried in an oven at 60 °C for 30 min and then cured at 150 °C for 3 min.

Characterization

FT-IR

The phthalocyanine green aluminum pigment (PGAP) polymer-encapsulated PGAP, and phthalocyanine green G were characterized by FT-IR (NICOLET iS50, scan 400–4000 cm^{-1}). Smart iTX device equipped with AR-coated diamond crystal having interferometer speed of 1.0 cm/s. OMNIC^{TM} software was used to obtain the spectral images with a pixel size of 1.56 × 1.56 μm in four scans per pixel at a spectral resolution of 4 cm^{-1} in attenuated total reflectance (ATR) mode where 32 scans per sample were averaged to obtain the spectral images. A non-destructive sample preparation method was used where samples were placed into the diamond plate, and the Smart iTX pressure tower was adjusted to ensure a consistent contact between the plate and the sample. The ambient temperature and relative humidity for the spectrometer were set between 18 and 25 °C, and less than 40 %, respectively, after which the spectra were acquired in ATR mode.

Thermo-gravimetric (TGA) analyses

Thermo-gravimetric (TGA) analyses were performed using TG apparatus (TGA/SDTA851e, Mettler Toledo instrument co., LTD, Switzerland) with 10 °C/min ramp from 25 to 700 °C.

Anti-corrosion

Anti-corrosive stability of aluminum pigment was measured using the displacement method described by Zhang et al., [9]. 1 g of Al samples were immersed in 250 mL water with pH 1 and 12, respectively, at 25 ± 2 °C for 168 h. The amount of gas evolved was measured during the

exposure time. The less the volume of gas evolved, the better the anti-corrosion performance.

Scanning electron microscopy (SEM)

Surface morphology of the samples was observed using Scanning Electron Microscope (Hitachi Model S-3200H) equipped with an STS X-Stream Imaging System.

Transmission electron microscopy (TEM)

TEM photograph was obtained using JEOL-1200EXII microscope (JEOL Ltd., Tokyo, Japan) operating at 80 keV equipped with a high-resolution Tietz F224 digital camera located below the imaging screen with a beam blanker acting as the camera shutter under a 120,000 magnification. Droplets of finely dispersed samples were dropped onto a TEM copper grid, and the solvent was evaporated at room temperature.

X-ray photoelectron spectroscopy

XPS was carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg Kα radiation (hv = 1253.6 eV) and Al Kα radiation (hv = 1486.6 eV). The X-ray anode was run at 250 W, and the high voltage was kept at 14.0 kV with a detection angle at 54°. The pass energy was fixed at 23.5, 46.95 or 93.90 eV. The base pressure of the analyzer chamber was 5×10^{-8} Pa. The sample was pressed directly into a self-supported disk (10 × 10 mm) and mounted on a sample holder and then transferred into the analyzer chamber. The whole spectra [0–1100 (1200) eV] and the narrow spectra of all the elements with much high resolution were both recorded using RBD 147 interface (RBD Enterprises, USA) through the AugerScan 3.21 software. Binding energies were calibrated using the containment carbon (C1s = 284.6 eV) which is not included in the data. The data analysis was carried out using the RBD AugerScan 3.21 software provided by RBD Enterprises.

Pigment dispersion (milling)

The pigment was dispersed using bead mill Mini Zeta-03-E NETZSCH Grinding & Dispersing Machine (Germany) at 1800 r/m for 2 h.

Particle size

Particle size (D) and the particle size distribution were determined by dynamic light scattering method (DLS) with Nano ZS90 (Malvern Instruments Co., Ltd., England) at 25 °C.

Adhesive properties

The adhesion properties of the samples were evaluated by peel test. Peel test was carried out using the method described by Gao et al. [26]. The weight of aluminum pigments pulled off was measured by calculating the weight difference of the pre- and post-peeled tape using Eq. 3.

$$W_p = A_0 - A_1 \quad (1)$$

where W_p is the weight of aluminum pigments fallen off from coating during peel test, A_0 represents the original weight of the board after drying before peeling the adhesive tape off, and A_1 represents the weight of the board after the adhesive tape was peeled off.

Color performance

The colorimetric values of the samples in the CIE lab color space were measured on a Color-Eye automatic differential colorimeter (Xrite-8400, X-Rite Color Management Co., Ltd., USA) under illuminant D65 with the CIE 1964 Standard Observers, and the color strength (K/S) of the coated fabrics was determined using Kubelka–Munk equation.

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \quad (2)$$

where R defines the relationship between the spectral reflectance of the sample and its absorbance coefficient (K) and scattering coefficient (S).

The rubbing and washing fastness properties of the coated fabrics were evaluated according to the standard method GB/T 3921-2008 and GB/T3922-1995, respectively.

Coating thickness

Coating thickness was measured with Paramount thickness tester precision gauge according to the standard method ASTM D1777—96 (2011).

Ultraviolet protection factor (UPF)

Ultraviolet protection factor was measured using Cary 50 UV/Vis spectrophotometer (varian made in Australia). The UPF of the samples was evaluated according to the Australian/New Zealand Standard AS/NZS 4399:1996. UPF was calculated using Eq. (3).

$$\mathrm{UPF} = \frac{\int_{280}^{400} E_\lambda \times S_\lambda \times \mathrm{d}\lambda}{\int_{280}^{400} E_\lambda \times S_\lambda \times \mathrm{d}\lambda} \quad (3)$$

where S_λ is erythema action spectrum, E_λ is solar irradiance, d_λ is wavelength interval in nm, and T_λ is spectral transmittance of the specimen.

Fabric handle

The softness of coated cotton fabrics was evaluated according to the Kawabata Evaluation System for Fabrics (KES-FB) on a handle instrument (KES-FB2, Kato Giken Co., Ltd. Japan).

Results and discussion

Preparation of colored aluminum pigment

Coloration of aluminum pigment followed a three-step approach where finely dispersed copper phthalocyanine green G pigment reacted with the ammonium ion ($NH4^+$) present in Silane Si–602 at very high pressures during the milling process. During this process, the labile chlorine atoms underwent a nucleophilic substitution with the amine groups (NH_2) of Silane Si-602 to ensure strong coupling effect with the copper phthalocyanine green G pigment. Secondly, the aluminum pigment reacted with polyphosphoric acid radical to form aluminum phosphate (AlPO4) on its surface [27]. A mixture of the aluminum phosphate and the modified phthalocyanine green pigment created a link at the nitrogen monohydride (NH) region of the coupling age because, the ammonium ions combined with the organic radical to form aluminum nitrogen phosphate [Al-N(PO_3)] [28]. This reaction created a unique compound between the aluminum phosphate and the modified phthalocyanine green pigment leading to the formation of colored aluminum pigment as shown in scheme 1. To confirm this reaction, a high-resolution X-ray photoelectron spectroscopy (XPS) of "as received aluminum pigment" and phthalocyanine green aluminum pigment was taken, and the results are shown in Fig. 2. XPS is a surface-sensitive quantitative spectroscopic technique that measures the elemental compositions at parts-per-thousand range, empirical formula, chemical and electronic state of the elements that exist within a composite. The XPS spectra were obtained by irradiating samples with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons that escaped from the top 0 to 10 nm of the samples ("as received aluminum pigment and PGAP") analyzed.

It can be seen from Fig. 2 that "as received aluminum" pigment showed doublet peaks O 1s and Al 2p with maximum peak intensities of approximately 40,000 and 21,000 at the binding energies of 536.02 and 535.69 eV, respectively, compared to PGAP which showed peaks for compounds present in the matrix but at lower intensities and different binding energies even for O 1s and Al 2p at approximately 34,000 and 4500 at binding energies of 533.97 and 537.25 eV. Besides these chemical shifts, copper phthalocyanine G; denoted as C.G 1s and phosphate compounds, also denoted as N(PO_3)2p3 were clearly shown in colored phthalocyanine green aluminum pigment (Fig. 2b) which are conspicuously missing in "as received aluminum pigment".

To ensure good adhesion property of phosphate/pigment coating on the aluminum pigment (metallic core), radical polymerization was done to encapsulate phthalocyanine green aluminum pigment with a thin film of polymer where the monomers tend to form dimers and trimers and then grow into a complex film of colorless polymer over the entire surface of PGAP with constant supply of heat over time.

Surface morphology

SEM and TEM are 3D surface topographic analysis tools capable of zooming to low magnifications to locate interesting areas of specimens to high magnifications down to nanometer surface features. These techniques were adopted to characterize the surface properties of the colored aluminum pigments and the images are shown in Fig. 3.

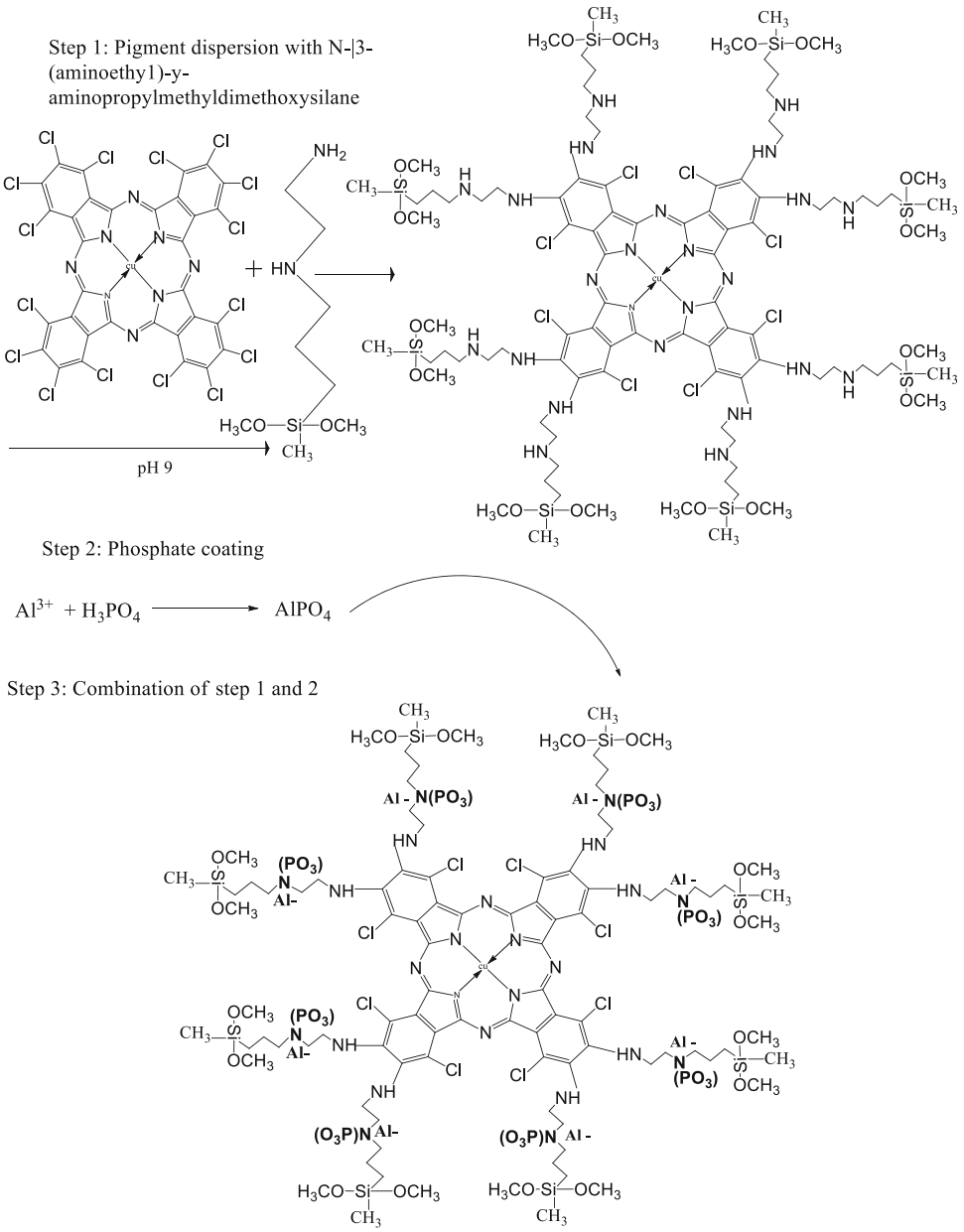
It can be seen that phthalocyanine green Al pigment (PGAP) (Fig. 3c, d) had a relatively thick layer of phosphate/pigment coatings compared to as received aluminum pigments (Fig. 3a, b). Also, it can be observed from (Fig. 3c) that colored phosphate on the surface of aluminum pigment was not very compact compared to the PAP (Fig. 3e, f). The polymer layer on the surface of PGAP gave PAP a relatively smoother surface suggesting a better barrier for corrosion resistance as a result of the radical polymerization. No significant difference can be seen in the TEM images of as received aluminum pigment (Fig. 3g), PGAP (Fig. 3h) and PAP (Fig. 3i), except what appears to be a smooth layer on the surface of PAP probably due to the encapsulated polymer layer.

FT-IR of colored aluminum pigment

FT-IR is a very useful surface characterization tool for single and multilayer films or matrix analysis. The spectra were acquired in ATR mode using Thermo Scientific Smart iTX device equipped with AR-coated diamond crystal plate.

Figure 4 shows the FT-IR spectra of PGAP and polymer-encapsulated PGAP and phthalocyanine green pigment. Minor broad shallow peak around 3432.37 cm^{-1} in phthalocyanine green pigment and PGAP though not obvious can be attributed to the O–H stretching vibration as

Scheme 1 Proposed reaction mechanism for preparation of phthalocyanine green aluminum pigment



a result of crystal water in phthalocyanine green but was not very prominent in polymer-encapsulated PAP (Fig. 4b). The minor peak recorded around 2926.79 cm^{-1} relating to C–H asymmetric stretching vibrations in phthalocyanine green pigment can be noticed in PGAP and polymer-encapsulated PGAP. The band observed in the FT-IR spectrum of PGAP and PAP around 1640.78, 1100, and 787.35 cm^{-1}, corresponds to the symmetric stretching mode of [PO4] [3] in $AlPO_4$ whereas the presence of peaks at 661.54 and 611.39 cm^{-1}, and the symmetric bending around 466.74 cm^{-1} indicates the presence of aluminum [29].

Characteristic absorbance band highlighted around 700.81 cm^{-1} could probably be due to out-of-plane ring bending of C=C stretching vibrations in phenyl ring in styrene unit, whereas the C=O wag at around 508.16 cm^{-1} [30] in PAP (Fig. 4b) could be attributed to the presence of other monomer units. More so, the characteristic band around 948.36 cm^{-1} in PGAP and PAP can be attributed to the out-of-plane bending mode of N–Cu and C–Cl in phthalocyanine green pigment [30].

Adhesive properties

The weight of aluminum pigments peeled off from coated board during peel test (W_p) is used to describe the adhesion property of aluminum pigments in coatings [24, 26]. High W_P values of aluminum pigments denote poor adhesion

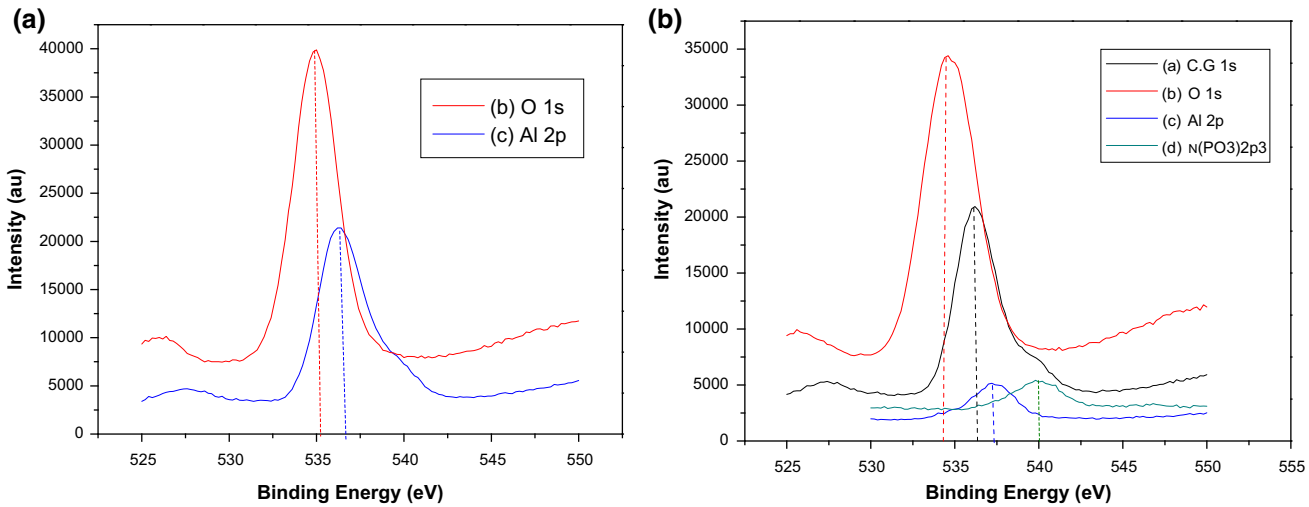


Fig. 2 High-resolution X-ray photoelectron spectra of (**a**) "as received aluminum pigment" (**b**) phthalocyanine green Al pigment (PGAP)

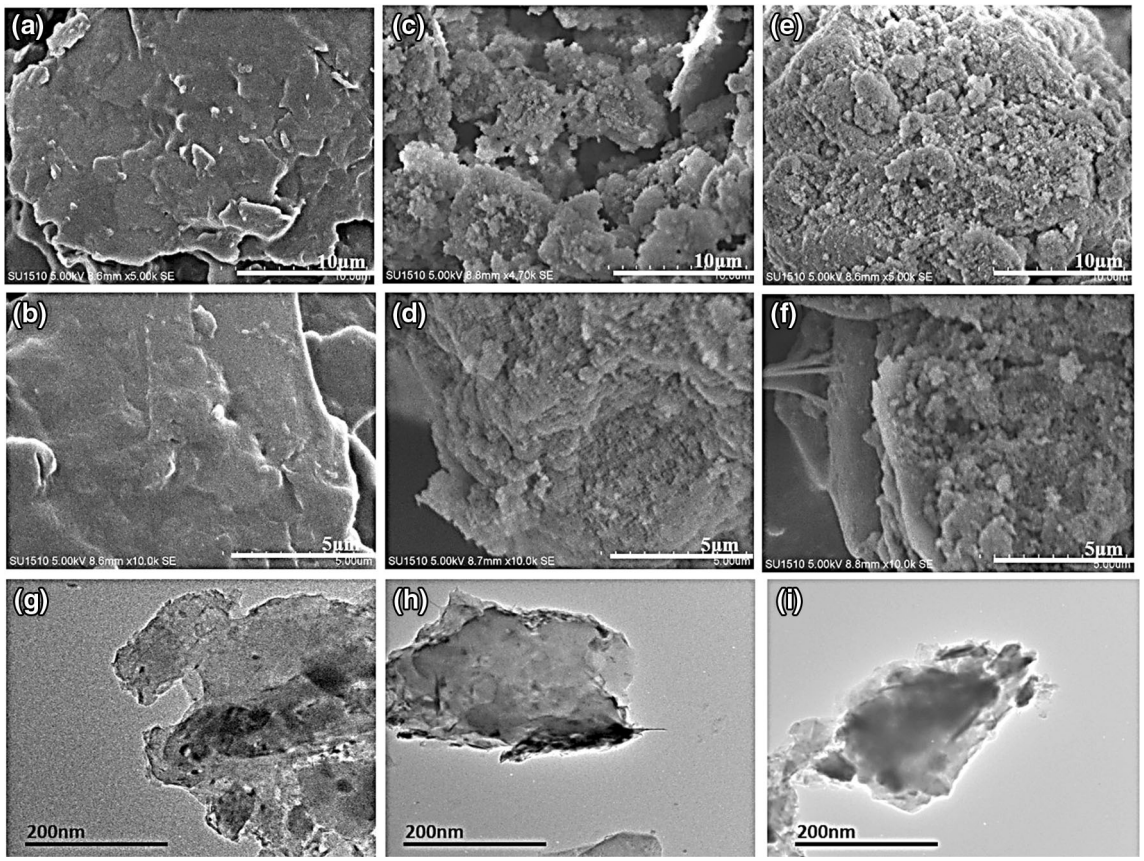


Fig. 3 SEM micrographs of (**a**, **b**) "as received Al pigment" (**c**, **d**) phthalocyanine green Al pigment (PGAP) (**e**, **f**) Polymer-encapsulated aluminum pigment (PAP) and TEM images of (**g**) as received aluminium pigment (**h**) phthalocyanine green Al pigment (PGAP) (**i**) polymer-encapsulated aluminum pigment (PAP)

performance. The adhesion efficiency of PGAP and PAP is shown in Fig. 5. PGAP had much poorer adhesion property (6.2 m g^{-2}) compared to PAP (0.5 m g^{-2}) probably due to the porous nature of the phosphate/pigment particles on the surface of the metallic core (aluminum pigment). The excellent adhesive property of PAP could be ascribed to the good adhesion force between the resin and the polymer film on the surface of PGAP. The polymer film on the

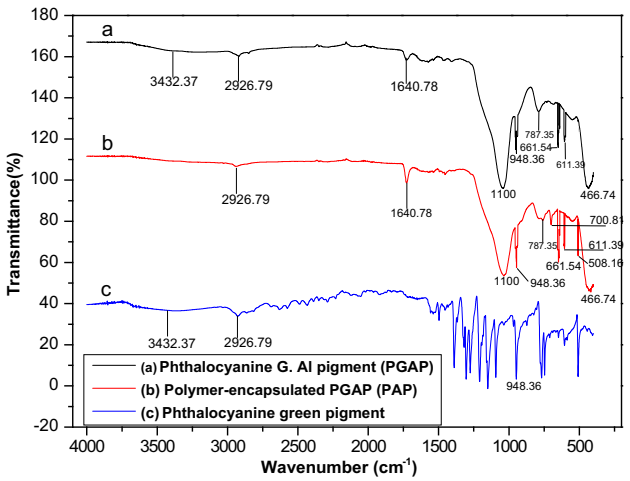


Fig. 4 FT-IR spectra of (*a*) phthalocyanine green Al pigment (PGAP) (*b*) polymer-encapsulated PGAP (PAP) (*c*) phthalocyanine green pigment

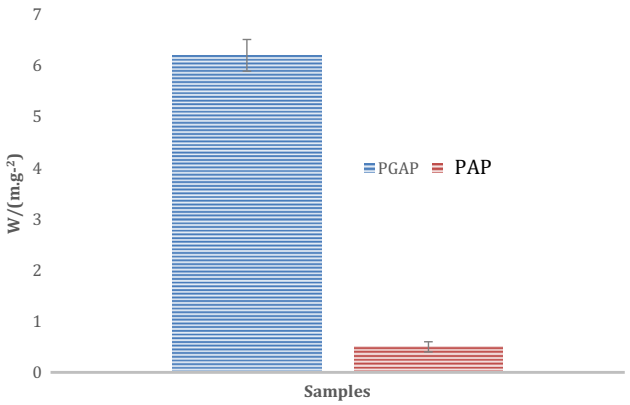


Fig. 5 Adhesion properties of (*a*) phthalocyanine green Al pigment (PGAP) (*b*) polymer-encapsulated aluminum pigment PGAP (PAP)

surface of PAP has, therefore, helped to minimize the problem of exfoliation usually experienced by conventionally colored aluminum pigments.

Anti-corrosive properties

The development of anti-corrosive and environmentally benign waterborne metallic colorants for wide variety of applications is very important. Metallic colorants especially for textiles applications must meet specific performance needs and as well satisfy the increasingly strict environmental regulation requirements. As a result, the anti-corrosive properties of the polymer-encapsulated Al pigment (PAP) meant for textiles applications were evaluated, and the results are shown in Fig. 6.

It can be seen that polymer-encapsulated phthalocyanine green Al pigment powder was highly stable in all circumstances under various conditions compared to the as received Al pigments and PGAP. It can be seen from Fig. 6a and b that H_2 started to evolve for as received aluminum pigment just after it was introduced to acid and alkaline conditions unlike PGAP which saw evolution of gas after 24 h at minimal magnitudes similar to results obtained by Abd El-Ghaffar et al. [23]. Similar observations were made when the paste was subjected to accelerated aging test at 50 ± 2 °C, pH 10 (Fig. 6c). Under the same conditions, PAP was highly stable even after 168 h. The gassing phenomenon witnessed in PGAP could be attributed to the gradual penetration of acid and alkali solutions through the phosphate layer onto the metallic core after long exposure forming $AlCl_3$ and $NaAlO_2$.

Particle size distribution

The mean particle size of "as received Al Pigment", PGAP, and polymer-encapsulated PGAP was measured by dynamic light scattering (DLS), and the result is shown in Fig. 7. It can be seen that the particle size distribution of all the three samples had an insignificant difference with an average particle size of 1772.5, 1957, and 1998.3 d nm for as received Al pigment, PGAP, and PAP, respectively, with "as received Al pigment" bigger than PGAP by 184.5 d nm possibly due to phosphate treatment and subsequent coloration by phthalocyanine green G. PAP particle size was also bigger than PGAP by approximately 41.3 d nm. The minimal increase in size of PAP could be attributed to the encapsulated polymer-layer coating on the surface of PGAP.

Thermal properties of polymer-encapsulated PGAP

Most solid polymeric materials experience both physical and chemical changes when heat is applied which usually results in undesirable changes to the properties of the material [31, 32]. This often results in thermal degradation or even decomposition where the action of heat or elevated temperatures on a material causes a loss of physical, mechanical, or electrical properties or at worse generate harmful gases [32]. Figure 8 shows the thermal properties of polymer-encapsulated phthalocyanine green aluminum pigment (PGAP).

It can be seen that "as received Al pigment" showed a gentle weight loss of approximately 0.5 % between 380 and 700 °C due to the decomposition of adsorbed water and oxide layer on its surface [26]. PGAP also experienced a consistent weight loss starting from approximately 250 °C until 700 °C. This phenomenon could be attributed to the decomposition of water, absolute ethanol, and the pigment on the surface of the aluminum pigment (metallic core) [12, 33]. Polymer-encapsulated PGAP, however, recorded

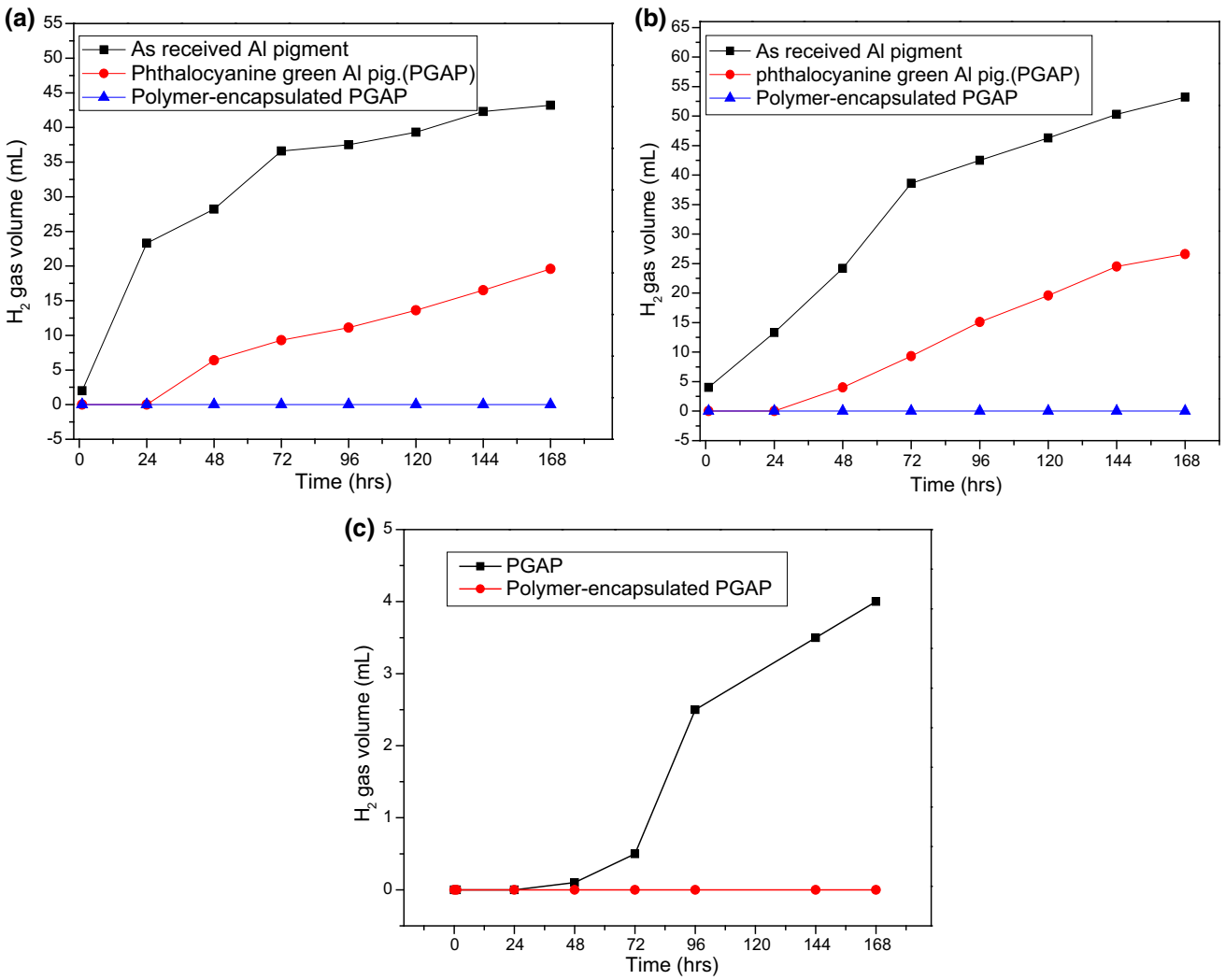


Fig. 6 Anti-corrosive stability of aluminum pigments in (**a**) acidic condition 25 ± 2 °C, pH 1 (**b**) alkaline condition 25 ± 2 °C, pH 12, (**c**) paste at 50 ± 2 °C, pH 10

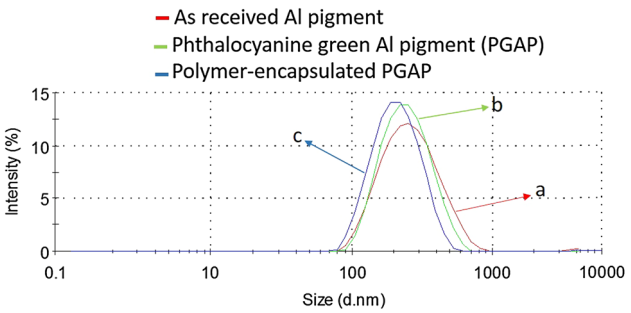


Fig. 7 Particle size distribution of (*a*) as received Al pigment (*b*) phthalocyanine green Al pigment (PGAP) (*c*) Polymer-encapsulated PGAP

a much faster and higher rate of decomposition due to the reduced thermal stability of the encapsulated polymer at high temperature [34].

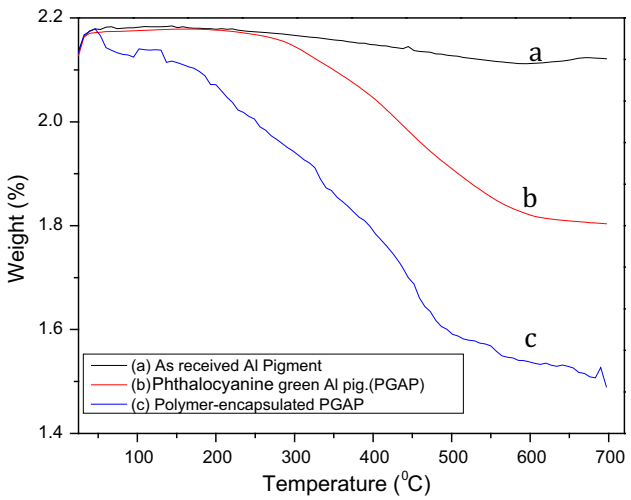


Fig. 8 Thermal properties of (*a*) "as received aluminum pigment" (*b*) phthalocyanine green aluminum pigment (PGAP) (*c*) polymer-encapsulated PGAP (PAP)

Table 1 Effect of polymer-encapsulated aluminum pigment (PAP) coating on color performance and handle of cotton fabrics

Polymer coating (%)	CT[a] (mm)	*K*/*S* value	λ_{max} (nm)	Rubbing fastness		Washing fastness		Handle
				Dry	Wet	Changing	Staining	
None		7.96	520	3	3	3–4	2–3	Softest
5		7.84	520	4	4	4–5	3–4	Softer
10		7.27	520	5	5	5	5	Soft
15		6.54	520	5	5	5	5	Poor
20		5.02	520	5	5	5	5	Poorer

CT coating thickness

[a] Coating was done on cotton fabric with thickness 0.21 mm

Color performance

Table 1 shows the effect of polymer coatings (monomer mass by weight of PGAP) on the color performance of polymer-encapsulated PGAP-coated fabrics. It can be seen that the *K*/*S* value decreased marginally as the coating thickness increased from 5 to 10 %. Beyond 10 %, however, the *K*/*S* value was adversely affected, but the λ_{max} remained fixed at 520 nm indicating that the hue was not affected except the considerable reduction in color strength (*K*/*S*). It can also be seen from Table 1 that PAP coated cotton fabric had good rubbing and washing fastness irrespective of the percentage polymer coating unlike PGAP which does not have polymer coating. The excellent rubbing and washing fastness could be attributed to the presence of polymer layer on the surface of PGAP even when the same amount of binder was used. The handle test indicates that the polymer coating had some negative effect on the handle of coated cotton fabrics because, as the percentage of monomer content increased, the handle was invariably affected as can be seen from Table 1.

Ultraviolet protection factor (UPF)

Regular and lengthy exposure to ultraviolet rays (UVA 400–320 nm, UVB 320–290 nm) can damage the immune system and cause skin diseases like erythema and skin burns, hence the need for UV protective clothing [34–36]. Cotton fabric was coated with polymer-encapsulated phthalocyanine green aluminum pigment, and the UPF was measured. Per the Australia/New Zealand standards AS/NZS 4399:1996, fabrics are considered to possess excellent UPF when they attain an average of 50 + UV rate; the greater the UPF, the better the UV protection.

It can be seen from Table 2 that UPF improved from 85.56 to 220.38 as coating thickness increased from 0.02 to 0.06 mm indicating that UPF of polymer-encapsulated phthalocyanine green aluminum pigment-coated cotton fabrics had excellent UV protection irrespective of the coating thickness similar to the results obtained in our previous findings [34]; meanwhile, handle of coated fabrics appeared compromised as the coating thickness increased beyond 0.04. The excellent UPF of polymer-encapsulated phthalocyanine green aluminum pigment-coated cotton fabrics could be attributed to the metallic core and excellent hiding power of the colored/polymer matrix.

Table 2 UPF of polymer-encapsulated phthalocyanine green aluminum pigment coated cotton fabrics

C.T. (mm)[a]	UPF	UPF class	Handle
0	8.66	No class	Softest
0.02	85.56	Excellent	Softer
0.04	161.21	Excellent	Soft
0.06	220.38	Excellent	Poor

Thickness of cotton fabric 0.21 mm, Cotton fabric was used

[a] C.T. means coating thickness

Conclusion

Polymer-encapsulated phthalocyanine green aluminum pigment was prepared via combined inorganic acid radical/radical polymerization method and was characterized. The colored aluminum pigment was applied on cotton fabrics and its washing and rubbing fastness were evaluated according to the internationally accepted standards. The polymer-encapsulated phthalocyanine green aluminum pigment had good washing and rubbing fastness compared to non-encapsulated type, but the handle and *K*/*S* values were compromised as the encapsulation monomer content (by 100 % weight of PGAP) increased beyond 10 %. TGA results showed that its thermal stability was minimally compromised. Polymer-encapsulated PGAP had excellent UPF irrespective of the coating thickness.

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Compliance with ethical standards

Conflict of interest The authors declare no competing financial interest for this research work.

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